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Palladium-Assisted Aromatic Metamorphosis of Dibenzothiophenes to Triphenylenes

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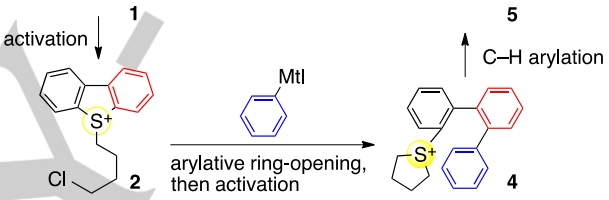
Abstract: By inventing a couple of new palladium-catalyzed reactions of aromatic sulfur compounds, dibenzothiophenes have become convertible into triphenylenes in four steps. This aromatic metamorphosis consists of 1) 4-chlorobutylation of dibenzothiophenes to form the corresponding sulfonium salts, 2) palladium-catalyzed arylative ring-opening of the sulfonium salts with sodium tetraarylborates, 3) intramolecular S_N2 reaction to form terarylyl sulfonium salts, and 4) palladium-catalyzed intramolecular C-S/C-H coupling via electrophilic palladation. Symmetrical as well as unsymmetrical triphenylenes of interest are synthesized in a tailor-made fashion in satisfactory overall yields, up to 73% in four steps. Multisubstituted triphenylenes are synthesized in a controlled manner alternatively from dibenzothiophene sulfonium salts prepared from 2-arylphenyl sulfoxides via Tf_2O-mediated cyclization.

Aromatic rings hold a central position in organic chemistry to govern the fundamental nature of countless aromatic compounds. Aromatic rings are generally stable and thus unbreakable except under harsh or special conditions. Converting an aromatic ring into a different aromatic ring is naturally challenging and has not been regarded as a general protocol.[1] For the last decade, transition metal catalysis has been developing to realize such conversions. Specifically, triazoles and related high-energy triazaarenes undergo catalytic denitrogenative transannulation with unsaturated compounds such as alkynes and nitriles to afford other aromatic systems.[2] There still remains ample room to develop novel strategies that realize conversions of aromatic rings into other aromatic systems with the aid of catalysts.

Sulfur-containing heteroaromatic skeletons such as thiophene are found widely in bioactive compounds and organic electronics as well as abundantly in unrefined oils.[3] Breaking thiophenes catalytically is usually difficult because sulfur species strongly poison transition metal catalysts. Although desulfurizative hydrogenation is an important heterogeneous catalytic process in oil refinery,[4] there are no reports on the catalytic conversions of thiophene units into other aromatic molecules.[5,6] Here we report a strategy for aromatic metamorphosis of dibenzothiophenes to triphenylenes with the aid of palladium catalysis. Triphenylenes have been attracting increasing attention due to their wide applications in liquid crystals, OLEDs, and photoconducting and optical data storage devices.[7] However, tailor-made synthesis of multisubstituted triphenylenes remains a challenge because of their symmetric and planar structures.[8,9]

Our strategy begins with activation of dibenzothiophene **1** to sulfonium salt **2** with diminishing the Lewis basicity of the sulfur atom (Scheme 1). Activated sulfonium salt **2** had been expected to undergo smooth cross-coupling with an aryl nucleophile.[10–12] The ring-opening product, 4-chlorobutyl terarylyl sulfide **3**, would be activated again through the formation of cyclic sulfonium salt **4**. Intramolecular C-H arylation of **4** should finalize our aromatic metamorphosis although there are no reports on catalytic C-H arylation[13] with an aromatic sulfur compound as an electrophilic partner.



Scheme 1. Strategy for aromatic metamorphosis from dibenzothiophenes to triphenylenes

The first step is readily achieved through $AgBF_4$-mediated S_N2 reaction[14] of dibenzothiophenes with 1-halo-4-chlorobutane. Simple dibenzothiophene (**1a**) reacted smoothly with 1-bromo-4-chlorobutane (eq 1). A variety of sulfonium salts **2** were obtained in high yields, especially with the more reactive 1-iodo-4-chlorobutane (Chart S1 in Supporting Information (SI)).

We next examined arylative ring-opening of **2**. However, **2** seriously suffured from rapid dealkylative decomposition owing to the high leaving group ability of the dibenzothiophene unit. Typical Suzuki-Miyaura or Migita-Kosugi-Stille conditions were ineffective, providing **1a** as the unwanted main product (See SI for details). The former required basic conditions that are not compatible with **2**, and the latter led to direct dealkylation reaction of **2** with a phenyltin reagent. These unsuccessful results suggested that desired arylmetal species should have exquisite reactivity to transfer its aryl group to palladium smoothly without the aid of an additional base as well as to remain unreactive toward sulfonium salt **2**. With this guideline in mind, we eventually devised a combination of sodium tetraarylborates[15] and $Pd(PtBu_3)_2$ catalyst[16] to achieve the expected transformation under mild additive-free conditions (Table 1). A variety of tetraarylborates participated in the arylative ring-opening. All the reactions went to completion within 45 min at 35 ˚C, which highlights the high efficiency of the ring-opening.

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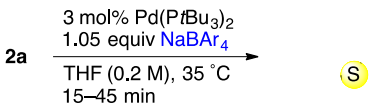
Supporting information for this article is given via a link at the end of the document.

Chart 1 represents the scope of dibenzothiophene sulfonium salts. The ring-opening was powerful enough to yield highly crowded **3l** and **3n** as well as quinquephenyl **3k**. Unsymmetrical **2f** underwent regioselective ring-opening at the less hindered C–S bond to form **3o** exclusively. This kinetic control also operated for benzonaphthothiophenes **2g–i** albeit with modest regioselectivities.[17]

Table 1. Arylative ring-opening of **2a** with $NaBAr_4$.



R	3	yield [%]	R	3	yield [%]
H	**3a**	81	4-F	**3f**	88
3-Me	**3b**	79	4-Cl	**3g**	77
4-Me	**3c**	80	3,4-OCH_2O	**3h**	84
3-MeO	**3d**	89	(2-naphthyl)	**3i**	73
4-MeO	**3e**	83	4-CHO[a]	**3j**	88

[a] $NaB[C_6H_4$-4-$CH(OMe)_2]_4$ was used. **3j** was obtained after hydrolysis with I_2 in aqueous acetone.

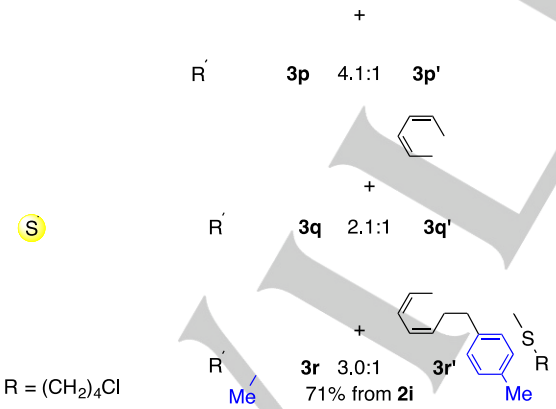
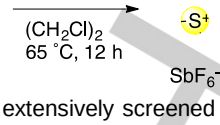


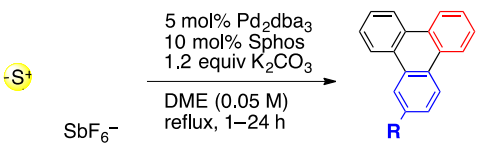
Chart 1. Products of arylative ring-opening of **2b–i**

Treatment of **3** with $AgSbF_6$ achieved highly efficient S_N2 cyclization of the corresponding terarylyl sulfonium salts **4** (eq 2 and Chart S2 in SI).



With **4** in hand, we extensively screened reaction conditions to achieve the final intramolecular C-H arylation (See SI for details). Luckily, a Pd/Sphos catalyst[18] has proved to be uniquely effective to generate triphenylenes **5** (Table 2, Chart 2, Table S2, and Chart S3). This is a rare example of C-H arylation by using organosulfur compounds as electrophilic arylating agents.[19] The reactions are generally efficient, furnishing the desired triphenylenes **5** in high to excellent yields. The four-step overall yields are satisfactory in most cases. The electronic nature of a substituent at the 4 position has little effect on the reaction efficiency (Table 2). A formyl group was compatible under the reaction conditions to form **5j**. The cyclization reactions of 3-substituted substrates **4b**, **4d**, **4h**, and **4i** pose a regioselective issue (Chart 2 and Chart S3). The regioselectivity is broadly in favor of the formation of the more congested triphenylenes. Notably, the cyclization of 3,4-methylenedioxy-substituted **4h** yielded **5h** with exclusive regioselectivity. The regioselectivity of naphthyl-derived **5i/5i'** was as high as 4.8:1 while those of **5b/5b'** and **5d/5d'** were almost negligible. Steric repulsions around the sulfur atom in **4l**, **4n**, and **4o** have no influence on the efficiency of the cyclization. In contrast, **5m** was obtained in only 22% yield along with elimination product **3m'** probably because of the outer-sphere steric repulsion in the binaphthyl backbones. The reaction of the isomeric mixture of **4p/4p'** led to the convergent formation of **5i**. Similarly, the mixture of **4q/4q'** converged into the sole product **5i'**. By recalling that a mixture of **5i/5i'** was obtained from **4i**, well-designed synthetic pathways would offer tailor-made synthesis of properly substituted triphenylenes.

Table 2. Palladium-catalyzed cyclization of **4**.



R	5	yield from **4** [%]	overall yield from **1** [%]
H	**5a**	92	70
Me	**5c**	89	66
MeO[a]	**5e**	98	73
F	**5f**	98	70
Cl	**5g**	84	54
CHO	**5j**	86	52

[a] 6 mol% Pd_2dba_3 and 12 mol% Sphos.

To clarify the reaction mechanism for the C–H arylation process, *ortho*-monodeuterated **4a-*d*** was prepared and subjected to the cyclization conditions (Scheme 2). A half of the deuterium proved to remain in the product and only small kinetic

isotope effect was observed. This result indicates that the reaction mechanism would include oxidative addition of the C(sp^2)–S bond to form the corresponding cationic arylpalladium intermediate **6**, which would then undergo electrophilic aromatic substitution via **7** for the C–H palladation step.[13,20–22]

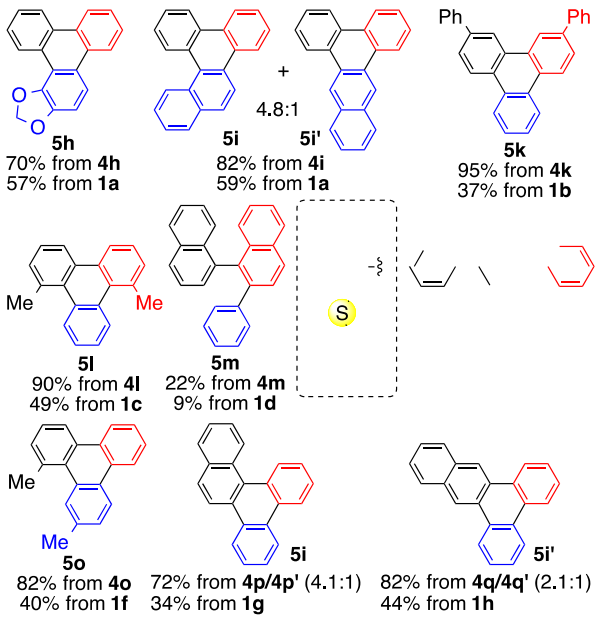
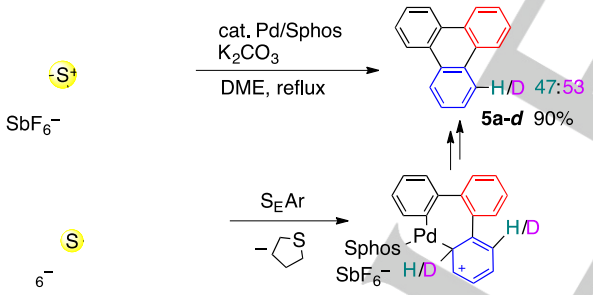


Chart 2. Triphenylene products **5h**, **5i**, **5k**–**o**. Conditions are described in Table 2. For **4h**, 10 mol% Pd_2dba_3 and 20 mol% Sphos were used.



Scheme 2. Deuterium-labeling experiment

Dibenzothiophene sulfonium salts were alternatively accessible by the cyclization of 2-arylphenyl sulfoxide under Pummerer-like conditions.[23] Sulfoxides **8**, readily prepared by cross-coupling biaryl synthesis, underwent Tf_2O-mediated electrophilic cyclization to provide **9** efficiently (Chart 3. See Scheme S4-6 in SI for details). Sulfonium triflates **9** were converted to triphenylenes **10** in good overall yields in five steps from **8**. This strategy will be useful for synthesizing multisubstituted triphenylenes in precisely controlled manners.

In conclusion, we have achieved aromatic metamorphosis of dibenzothiophenes into triphenylenes by inventing a couple of new palladium-catalyzed arylation. Due to the invaluable roles that aromatic cores play, aromatic metamorphosis would be a game-changing strategy in organic chemistry. Investigations to develop new aromatic metamorphosis are underway in our laboratory.

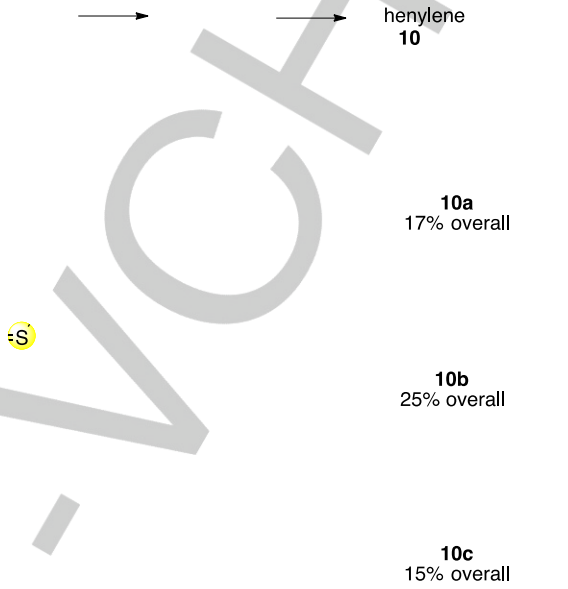


Chart 3. Multisubstituted triphenylenes through Tf_2O-mediated sulfonium formation. a) 2 equiv Tf_2O, $(CH_2Cl)_2$, 25 °C, 15–30 min; b) Conditions in Table 1, in eq 2, and then in Table 2.

Acknowledgement

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Keywords: palladium • sulfur • C-H arylation • C-S cleavage • cross-coupling

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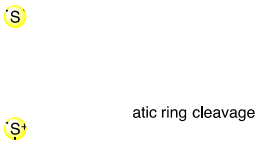

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Palladium-Assisted Aromatic Metamorphosis of Dibenzothiophenes to Triphenylenes

By inventing a couple of new palladium-catalyzed arylation, we have achieved aromatic metamorphosis of dibenzothiophenes into triphenylenes. Symmetrical as well as unsymmetrical triphenylenes of interest are synthesized in a tailor-made fashion in satisfactory overall yields.